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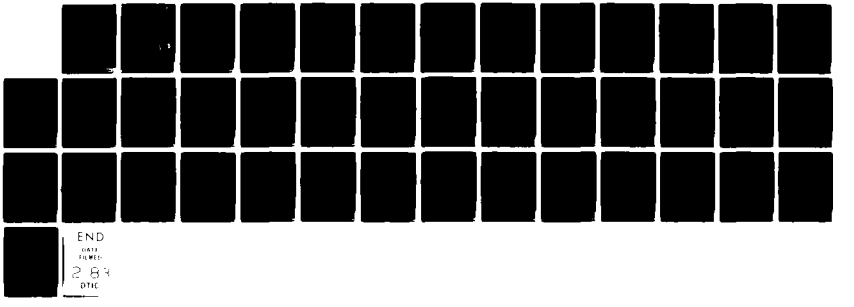

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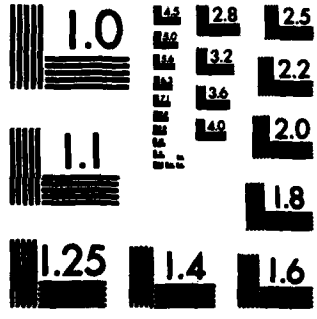

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The Use of Infrared Methods to Study Polymer Interfaces

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The surfaces of polymers and interfacial reactions between polymers and other materials are of much interest to the coatings and adhesive industries. There are many techniques which are available to study these surfaces, but none can yield as much information about the chemical nature of polymer surfaces as infrared spectroscopy. In the past, such studies were severely limited by a lack of specialized surface-specific IR techniques for the study of opaque samples or samples with small quantities (monolayer amount) of surface species. With the development of Fourier transform infrared spectroscopy (FT-IR), this

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THE USE OF INFRARED METHODS TO STUDY POLYMER INTERFACES

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I. Introduction

The surfaces of polymers and interfacial reactions between polymers and other materials are of much interest to the coatings and adhesive industries. There are many techniques (1-4) which are available to study these surfaces, but none can yield as much information about the chemical nature of polymer surfaces as infrared spectroscopy. In the past, such studies were severely limited by a lack of specialized surface-specific IR techniques for the study of opaque samples or samples with small quantities (monolayer amount) of surface species. With the development of Fourier Transform Infrared Spectroscopy (FT-IR), this situation has changed. The increased sensitivity, selectivity, energy throughput, reproducibility, and computerization of the FT-IR technique now allow the spectroscopists to probe the chemical nature of polymer surfaces routinely.

It is the purpose of this article to describe the recent developments in the field of FT-IR spectroscopy which have increased the understanding of the surface properties of polymers. Particular attention is paid to the new techniques that evolved with the development of FT-IR. The theory of each technique is discussed as well as their applications.

Throughout the following discussion of the various infrared techniques, Figures 1 and 2 will be helpful in allowing one to visualize and understand the theoretical basis of each of these techniques. Figure 1 is an overview of the physical processes that affect light as it passes through two materials of different refractive indexes as a function of the angle of incidence. Light is transmitted at a 90° angle of incidence, reflected and refracted at $\theta < \theta_c$, or totally reflected at $\theta > \theta_c$. Figure 2 shows the experimental set up of all the techniques discussed; PAS, specular reflection, RA, multiple RA, Emission, IRS, multiple IRS, transmission,

and diffuse reflectance. In each case the sample is represented by slanted lines. When considering each technique separately, these Figures will be cited for comparison purposes.

II. Photoacoustic Spectroscopy

The development of FT-IR Spectroscopy has renewed interest in an old technique developed in 1881 (5-7) to study solid samples in the mid-IR region of the spectrum called Photoacoustic Spectroscopy (PAS). Any sample: solid, liquid, or gas can be studied using PAS, however PAS has little advantage over conventional infrared methods for generating the spectra of liquids and gases. This new technique, FT-IR-PAS, has the advantage that no sample preparation is required before the spectrum can be obtained. In this respect, the PAS technique is comparable to the diffuse reflectance technique (8-10), but has the advantage that the sample can be analyzed "as received". A PAS study requires a small amount of the sample (1 ms). However, the SNR is very low, making long scan times necessary to obtain good spectra. The low penetration depth of PAS also makes it an ideal technique to study surface phenomena and surface interactions between coatings and solids.

The photoacoustic effect is based on the generation of sound when a sample is exposed to modulated light. The sample is placed in a closed cell containing a coupling gas (helium or argon) or air and a very sensitive microphone. If the sample absorbs any of the modulated light which is controlled by the mirror velocity of the interferogram of the FT-IR, its internal energy levels are excited. Due to the modulation of the light, the heating of the sample is periodic in nature. Upon de-excitation of the internal energy levels, a portion of the absorbed energy is transformed to heat. This periodic heat flow causes pressure fluctuations within the cell which are detected by a sensitive microphone creating the PA signal. Reflected or scattered light not absorbed by the sample does not contribute to the

PA effect. Such samples are conveniently studied by PAS.

The theory of PAS has been updated by Rosencwsis and Gersho (11), they discuss six special cases of samples optically thick and thin, and Rosencwsis has recently written a book on the topic (12). The basic requirement for obtaining a PA spectra is that the optical absorption length μ_β of the sample must be similar to or larger than the thermal diffusion length μ_s. This requirement allows optically dense samples to be studied by PAS. For quantitative studies it is important to consider saturation and scattering effects. Saturation will occur when the optical absorption length approaches the thermal diffusion length of the sample. This is not a serious problem in the infrared region of the spectrum, however. The light scattering problem, at first thought to be unimportant in PAS, has recently been re-evaluated (8,10,13). Scattering shows a tendency to increase the band intensities because the thermal diffusion path length to the surface is reduced (8). The penetration depth of the incident light is dependent upon the modulation frequency of the interferometer mirror. In general, the penetration depth has been found to be greater at low mirror velocities and much less at higher mirror velocities. At low mirror velocities saturation becomes a significant problem while at high mirror velocities the PA method can be used to probe surface phenomenon (9).

A PA sample cell is shown in Figure 2 (a). The window of the cell must be transparent to IR radiation and is usually made of KBr. There are several important factors to consider when designing PA cells to optimize the SNR (14). The SNR can be optimized by: 1) isolating the cell and microphone from any outside noise; 2) using different gases; 3) lowering the temperature (increase resolution); 4) minimizing any extraneous PA signal arising from the interaction of light with the walls of the cell; 5) modifying the microphone configuration; and 6) designing the cell to maximize PA signal for the type of sample to be studied.

Many of the applications of the PAS technique come from biological studies, (11,15). The following substrates have been studied by FT-IR-PAS: coal (8,9,16); silica (9,13,17-19); and alumina (20). The technique has also been applied to polymers (8,9,21-23). Studies by Low and Parodi (17,19) demonstrate that surface species can be detected on silica and alumina. When the silica sample is modified with a silane, the resulting PA spectra yields peaks which are assigned to surface Si-OH, Si-O-$SiHCl_2$, Si-H, and other bands. When alumina is modified by esterification, the Al-$OOCH_3$ peaks were clearly present in the resulting spectra. Rockley and Devin (16) have demonstrated the usefulness of the FT-IR-PAS technique to study the surfaces of aging coal samples. They were able to study the effects of oxidation of the coal samples. These examples illustrate that PAS is a very useful technique for studying the surfaces of many solid systems which are difficult to study by transmission methods.

Quantitative analysis using the PA method is difficult (24). This is due in part to the dependence of the signal amplitude on such sample properties as the thermal diffusion length, absorbance, and the various instrumental variables. Furthermore, light scattering has been found to significantly alter the intensity of the bands (8,10,13). Currently, most of the work involving PAS is qualitative and involves analysis of surfaces and polymer systems.

Unfortunately, much of the initial enthusiasm has been lost for this technique due to the low sensitivity of PAS and the difficulties in optimizing the experimental set-up for quantitative analysis. Yet FT-IR-PAS should be seriously considered along with the diffuse reflectance technique whenever difficult sample preparation are barriers to the IR analysis of solids. If the problems associated with quantitative analysis can be overcome, this technique has a bright future for the study of surfaces and interfaces in solids.

III. Infrared Reflection Techniques

In the past, there were two main classifications for reflection techniques, internal reflection (IRS) and external reflection spectroscopy (ERS). The internal reflection technique is also commonly referred to as multiple internal reflection (MIR), attenuated total reflection (ATR), or frustrated total reflection (FTR). The external reflection technique is most commonly referred to as reflection-absorption (RA) or sometimes specular reflection, but these two do not refer to the same process. Recently, a third reflection technique has been revived, diffuse reflectance.

The chemical changes which take place between polymers and metal surfaces or in chemical reactions that occur on the surface of metals can be studied nondestructively with the IRS or ERS techniques. The instrumental considerations for IR analysis are discussed (25,26) and apply to both types of instruments. Other reviews (26-34) also discuss these reflection techniques.

A. External Reflection

An External Reflection technique, RA, is useful for studying the structure of materials in contact with metal surfaces. The infrared absorption spectra of surface species and thin films on metal surfaces are obtained by reflection from the metal surface. The RA technique was developed by Francis and Ellison (35) and Greenler (36). Francis and Ellison (35) demonstrated that it is possible to study the molecular structure of monolayers adsorbed on the surface of polished metals.

When infrared radiation illuminates a metal surface, an electrical field arises near that surface. The magnitude of this electric field is determined by the angle of incidence of the radiation. At normal incidence the waves are phase shifted 180° and form a standing wave with a node very close to the metal surface. The result of this normal incidence is that very little interaction between the radia-

tion and the sample occurs (y component or parallel) so no IR spectrum is obtained. A similar trend is also observed for all angles of incidence when perpendicular polarized light is used. The phase shift for the component polarized parallel to the plane of incidence changes rapidly, however, at high angles of incidence. When the phase shifts change but are not 180° out of phase, an electric field is set up at the surface of the metal that has a sizable component normal (in the z direction) to the metal surface. The maximum interaction is obtained between the sample and the incident light at an angle of 88° (measured from the normal)(36). Sufficient interaction also occurs between the angles of 75° to 89° for absorbance bands to be seen in the IR spectrum. When polarized parallel radiation is used, only the dipole moments of the surface species which are normal (in the z direction) to the metal surface will interact with the electric field. This change gives rise to an IR spectrum. Practically no absorption bands are observed when polarized perpendicular radiation is used. This unique feature of RA has been used to study the orientation of Blodgett films of metal stearates on metal mirrors (35). A schematic diagram for a single reflection experiment is shown in Figure 2 (b).

Multiple reflections increase the signal strength in the RA technique. It would appear that the more reflections there are, the stronger the signal. This is not the case, however. The reflections in RA are not loss-less like in the ATR technique, which means the background decreases with each reflection causing a drop in the intensity of the radiation. Greenler (37) has demonstrated that the maximum (SNR) was obtained when the number of reflections reduced the background energy to 37% of its initial value. It was also found that the angle of incidence was not as critical when multiple reflections were used. The number of reflections is easily increased by reducing the distance between the two sample mirrors.

Greenler (38) has determined the optimum number of reflections for 19 different

metals. Taking into consideration all of the variables (angle of incidence, frequency of radiation, optical properties of the metal, etc.) the optimum number of reflections was calculated at two different frequencies (2100 and 500 cm^{-1}). It was found that a single reflection experiment produces absorbance bands that are generally greater than 60% of the optimum value obtainable if multiple reflections were used. Therefore, a multiple reflection device may add little to the RA spectra of most coatings on metal substrates.

RA spectroscopy can be used to study both thin films (monolayers and less) and relatively thick films (multilayer to 500Å). For thicker films a single reflection is usually sufficient. Generally, much thinner films are studied by the RA technique than are studied by the ATR technique. One important difference is that in RA spectroscopy the reflection is already built in since the sample is the film-substrate (metal) combination.

For optimum conditions, it has been shown (26,36) that a reflection spectrum of a thin film can be 10 to 50 times stronger than the corresponding transmission spectrum for the same film supported on a transparent substrate at normal incidence. Frequency shifts in the RA spectra for thin films have been reported. A theoretical discussion of this phenomenon has been reported for thin films on reflective surfaces (39). Bates (40) has demonstrated that the frequency of the absorption bands shift as a function of the angle of incidence with the RA technique. The effect of refractive index on the band shape and intensity are discussed (41).

The change in reflectance, ΔR, of a metal coated by a thin film is (42):

$$\Delta R = 1 - \frac{R}{R_o} = \frac{16\pi d k_2}{\lambda n_2^3} \frac{\sin^2\theta}{\cos\theta}$$

where R is the reflectivity of the metal, R_o is the reflectivity of the metal with a film on it, d is the film thickness, θ is the angle of incidence, n_2 is the re-

fractive index of the film and, k_2 is the absorption constant of the film (42).

$$\frac{k_2}{\lambda} = \frac{2.303\ \varepsilon c}{4\pi}$$

Where e is the absorptivity and c is the density of the absorbing species, ΔR reduces to

$$\Delta R = \frac{\varepsilon c d}{n_2^3}\ \frac{9.212\ \sin^2\theta}{\cos\theta}$$

for $0 \leq \theta \leq 80$. For thin films the change in reflectivity is small. Therefore proper experimental alignment must be used to obtain interpretable spectra.

In the past, most of the applications of RA-IR spectroscopy have dealt with the study of adsorbed species on metals. The most popular species has been the adsorption of carbon monoxide (CO) on various metals (43-53). These works indicate the sensitivity of the RA technique since most had submonolayer quantities of CO on the metal substrate and were obtained by a single reflection.

Particularly relevant to this review, are the examples of RA application to the study of polymers and surface coatings on metal substrates. Much of this work has been done by Boerio et al. (53-59) and involved the adsorption of silane coupling agents on metal substrates. Silanes are used as primers for metals to improve the adhesion of metals in contact with polymers. The RA technique is ideal for this type of study because the orientation and adsorption mechanism of the coupling agent can be probed.

Boerio and Chen (60) have used the RAS technique to study thin epoxy films on iron and copper mirrors. A 78 angle of incidence with six reflections off the copper mirror and two reflections off the iron mirror were used to obtain the spectra of the epoxy films. It was concluded that the epoxy molecules were adsorbed vertically to the surface through a single oxirane oxygen.

Chan and Allara (61) used RA to study the oxidation of a copper-polyethylene interface. Allara (26) used RA to study the oxidation of poly (1-butene) films on gold and copper. The RA technique has been used in combination with FT-IR spectrometers. The FT-IR-RAS technique (62) was used to study the depolymerization of poly (methyl methacrylate) on gold, nickel, and zinc surfaces. The depolymerization of the polymer was followed by observing changes in the PMMA C=O 1740 cm^{-1} band. The results indicate that the rate of the depolymerization process is influenced by the metal substrate, with the fastest rate on nickel and slowest on zinc. This study indicates that the chemical properties of thin films are much different from the chemical properties of bulk polymer samples.

FT-IR-RAS was used (39) to study the distortions that occur in the absorption spectra of thin polymer films (PMMA) on metals. The films ranged in thickness from 2 μm down to nearly monolayer coatings on gold and silicon surfaces. From this study several generalizations were made about band shifts and distortions of polymer films analysed with RA and compared to transmission spectra. These results are summarized as follows: 1) broad absorption bands are shifted much more than narrow bands; 2) for bands with small attenuation constants ($k < 0.1$) the RAS spectra closely resemble the transmission spectra except that the band intensities may not be the same; 3) the bands are always shifted to higher frequencies for very thin films; and 4) for similar bands in a spectrum, the distortion effects are greater in the higher frequency bands and the film thickness is increased.

Yoshida and Ishida (63) have taken advantage of the sensitivity of FT-IR-RAS to study the orientation of imidazoles on copper and gold mirrors. Imidazoles act as corrosion inhibitors when applied to metal surfaces. An example of the quality of the spectra obtained by the RAS technique is shown in Figure 3, which shows the spectra of undecylimidazole obtained by RA and transmission in KBr pellet form.

The RA spectrum shows the asymmetric CH_3 stretching band at 2955 cm^{-1}, the asymmetric CH_2 stretching band at 2925 cm^{-1}, and the CH out-of-plane bending band of imidazole at 763 cm^{-1} on gold. These bands have their dipole moments perpendicular to the gold surface. In contrast, the dipole moments of the NH stretching at 3077 cm^{-1}, the symmetric CH_2 stretching mode at 2850 cm^{-1}, the stretching and bending modes of the imidazole ring and CH_2 bending mode at 1578, 1470 cm^{-1} respectively are parallel to the gold surface because they only appear in the transmission spectrum of the film which has random orientation. From these results, it is deduced that the imidazole ring is adsorbed parallel to the surface along with the C-C bonds of the side chain oriented parallel to the gold surface. Similar results were obtained when the substrate was copper, but the mechanism was more complicated.

B. Internal Reflection Spectroscopy

Another popular reflection technique is IRS. The first applications of IRS were independently reported by Harrick (64) and Fahrenfort (65,66). Harrick (32) has developed the technique and discussed its theory and potential areas for application. The IRS technique is useful for studying the surface properties of many materials, polymers included, that can be brought into contact with the internal reflection element (IRE). Often these materials (rubbers, fibers, coatings, etc.) are difficult to study by transmission spectroscopy.

The basic principles of IRS are shown in Figures 1 and 2 (d and e). The samples are in optical contact with the IRE (prism). The IR radiation passes through the IRE and makes a total internal reflection at the surface of the sample as shown in Figure 1. The IRE is optically denser than the sample. When the angle of incidence exceeds the critical angle θ_c, total internal reflection takes place. The incident light forms a standing wave perpendicular to the interface between the two

surfaces. If the sample absorbs some of the radiation, the incident wave interacts with the sample and becomes attenuated (loses energy) giving rise to an ATR. The main difference between the IRS and RAS experiment is the location of the sample. In IRS, the sample is located on the opposite side of the interface from the incoming radiation.

Theoretically in the IRS technique the incident radiation is not lost as the number of reflections increase. In a properly designed system the energy remains constant regardless of the number of reflections. This is not the case in RA where the energy of the incident beam is lost to the metal. Therefore, multiple reflections can be used to enhance a very weak absorption band.

One of the most important considerations of IRS spectroscopy, and for the study of surfaces, is the ability to control the depth of penetration of the radiation into the sample. The depth of penetration is described (32) by equation [1]

$$d_p = \frac{\lambda_o}{2\pi n_1 (\sin^2\theta - n_{21}^2)^{\frac{1}{2}}} \qquad [1]$$

where d_p describes the distance required for the electric field to fall off to e^{-1} of its value at the surface, θ is the angle of incidence, n_{21} is the refractive index of the sample (n_2) divided by the refractive index of the IRE (n_1) and λ_o is the wavelength of radiation. Examination of equation [1] indicates that: 1) d_p increases linearly as the λ is increased which causes the absorption bands at long wavelengths to be distorted and 2) the d_p decreases as a) the angle of incidence is increased, b) as the refractive index (n_1) increases, and c) as the refractive index (n_2) decreases. The depth of penetration reaches a maximum at the critical angle of total internal reflection.

The most important aspect of the IRS experiment is the reflection elements (RE)

used. Various geometries are available such as trapezoids and parallelepipeds with fixed angle RE's. The radiation propagates the length by multiple reflection, where the number of reflections is given by

$$N = \frac{l}{t} \tan\theta$$

The RE can be a single pass system or a double pass system with the entrance and exit apertures at the same end. The variable angle RE's are very useful for changing spectral contrast and for investigating layers of various thicknesses by changing the depth of penetration. A variety of materials have been used for RE (32,67) with the most common of these being KRS-5 (thallium bromiodide), Si, Ge, Ge glass, ZnSe, and CaF_2. When multiple reflections are used, the nature of the RE's surface becomes very important. Special polishing and cleaning techniques (32,67) have been developed to insure proper finish and geometry of the RE. When multiple reflections are used to enhance absorption bands, energy losses can occur if the surface of the IRE is not polished and cleaned.

Surface contact between the sample and RE is one of the major problems of IRS. For hard, rough materials, the surface contact is the most difficult variable to accurately control. Soft flexible materials make excellent contact with the RE, but hard samples make only line or point contact. Thus the amount of pressure applied can cause changes in the absorption characteristics. But soft IRE's are easily scratched and lead to distortions in the spectra. Sample homogenity, position of the sample on the IRE surface (68), and area of the IRE coverage also affect the reproducibility of an IRS spectrum (69). For these reasons, it is very difficult to obtain quantitative results using the internal reflection technique.

Versatility is an asset of IRS. Unlike RA spectroscopy, any sample which can be brought into contact with the IRE and interacts with IR radiation can be studied

by the IRS technique. Thick and thin films can be studied. Also the sample can be adsorbed or coated on the RE plate. The problem of interference fringes which arise in the study of films by transmission IR does not occur when the IRS technique is employed (32).

The dependence of the reflectivity on the angle of incidence is shown in Figure 4 for both internal and external reflection for a specific set of conditions (32,70). In the case of parallel polarized radiation for external reflection, the reflectivity is zero at the Brewster's angle. There is a similar condition at the principle angle for internal reflection. The two are related as $\theta_p + \theta_b = 90°$. In the case of internal reflection, where the total reflection occurs above the critical angle, the reflectivity is 100% for both parallel and perpendicular polarized radiation. Figure 2 helps one to visualize the differences in reflectivity that arise when the two different reflection techniques are used.

IRS is most useful for the study of thin films on a thick substrate. Jakobsen (31) has studied several thin films on polymer surfaces such as rubbers, epoxies, PMMA on graphite, polyethylene, and an eye lens. An interesting application of ATR was to study the effect of abrasion on airplane tires of silicone modified unfilled rubber (SMR). The results indicate that the additive is lost and that isomerization of the double bonds may be the first step in the degradation caused by abrasion.

There are several recent examples of depth profile studies of polymer films (31,71-73). Coleman and Painter (72) studied the morphology and structure of polyurethane using the FT-IRS technique. The spectra of the various levels were obtained by subtraction of spectra obtained by varying the angle of incidence and using different IRE's. This study showed that two morphologies were present in polyurethane, one related to the surface and the other attributed to the bulk.

Sung et al (73) used FT-IR and barrier films of different thicknesses to study the morphological differences in segmented polyurethanes. This is one alternative to changing the angle of incidence or the IRE to change the depth of penetration. Jakobsen (31) studied the interaction of steric acid films on metal substrates to form metal salts as a function of film thickness. The angle of incidence was changed and the spectra obtained at two different angles were subtracted to yield the spectra of an intermediate layer. This approach can be used to characterize thin films up to the maximum depth of penetration of the IR radiation for each IRE used.

Molecular orientation studies can also be performed using the ATR technique. Takenaka et al (74) used polarized ATR to study the orientation of stearic acid films. The results show that the films are uniaxially oriented with respect to the z-axis and that the molecular orientation may become slightly more random as the thickness of the film is increased. More recently, Nakahara et al (75) applied the polarized ATR technique to study orientation of thin films. Seven anthraquinone derivatives with a varying number of stearylamino groups (1 or 2) at different positions were used. The results are consistent with previous findings employing other techniques that found the orientation of the anthraquinone was a function of both the number of substituents and the relative position. Care must be taken in these studies to insure that the surface of the IRE is of high quality. Surface roughness randomizes the dipole orientation of the spectra even if a polarizer is used (76). Sung (77) developed a new sampling technique to perform FT-ATR dichroism studies which measures the surface orientation of polymers (polypropylene) to approximately 1μm. This technique utilizes a symmetrical double-edged IRE. The sample holder can be rotated, eliminating the possibility of changing the contact area between the sample and IRE. This setup also eliminates the need to

correct the reflectivities to an internal absorption band which must be insensitive to orientation. When a uniaxially drawn polypropylene sample was tested, the results showed that the surface orientation was the same as the bulk. When an injection molded polypropylene sample was tested however, the results showed more orientation at the surface than the core. These results were confirmed by birefringence measurements.

The FT-ATR technique has sufficient sensitivity to study submonolayer quantities of materials coated on the IRE (32). Hartstein et al (47) was the first to demonstrate that the sensitivity of the ATR technique could be enhanced by the use of thin metal overlayers. The samples studied were monolayers of organic acids on silicon. The metals used were Ag or Au and were evaporated at room temperature after the monolayers were applied to a thickness of approximately 60Å. The maximum increase in the absorption which resulted from the use of the metal overlayers was by a factor of 20. It is believed that the enhancement arises from an increase in the electric field as a result of the electron resonances related to the metal deposited on the samples. This new technique increases the sensitivity of the ATR technique for the study of monolayer and submonolayer quantities of materials which absorb infrared radiation weakly.

The ATR technique has also been spplied to study an epoxy adhesive by Jakobsen (31). Titanium aircraft parts are bonded together by the epoxy adhesive. Two titanium pieces were joined by the epoxy and later pulled apart. FT-ATR was used to determine if the adhesive failure occurred at the interface between the titanium and epoxy or within the epoxy matrix. The results showed that the failure was between epoxy-epoxy bonds, not between epoxy-metal bonds, as both spectra of the titanium strips had the characteristic epoxy bands present.

C. Diffuse Reflectance Spectroscopy

With the improved sensitivity of FT-IR spectrometers, it is possible to obtain spectra through diffuse reflectance spectroscopy. Diffuse reflectance overcomes most of the disadvantages associated with KBr and mull techniques for solid and powdered samples or turbid solutions. Willey (78) developed an FT-IR spectrometer built solely for the purpose of collecting diffuse reflectance measurements. The mid-IR region was never developed because the same optical systems that were used in the UV and near IR regions were inefficient due to the insensitivity of the mid-IR detector.

The basic principle behind diffuse reflectance spectroscopy (79) is that light incident upon a solid or powdered surface will be diffusely scattered in all directions [see figure 2(f)]. The scattered light is collected with the proper optical setup and directed to the IR detector for analysis. The general theory which describes the diffuse reflectance process for powdered samples was developed by Kubelka and Munk (80,81). This theory relates the sample concentration to the scattered radiation intensity. The Kubelka-Munk (K-M) equation is usually written as:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{}$$

where R_∞ is the absolute reflectance of the layer, s is the scattering coefficient, and k is the molar absorption coefficient.

Griffiths (82) discussed the K-M theory of diffuse reflectance and demonstrated that in certain cases it can be used for quantitative studies. The theory predicts a linear relationship between the molar absorption coefficient and the maximum value of $f(R_\infty)$ for every peak, if s is held constant. The scattering coefficient, s, is dependent on the particle size of the sample and must be kept constant to obtain quantitative results. Therefore, the K-M formula can be rewritten as:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{c}{k'}$$

where c is the concentration, and k' depends on the particle size and the molar absorptivity of the sample by $k' = s/2.303\ e$. At high concentration ranges, however, the K-M function becomes nonlinear.

Diffuse reflectance spectra are usually generated by recording a single beam reference spectrum (KBr or KCl powder) and a single beam sample spectrum (either neat or diluted 95 to 99% with the alkali halide powder). The reflectance spectrum, R_∞, is produced by ratioing the sample with the reference spectrum. The K-M plot is easily generated. It is interesting to note that spectra of both powdered and solid samples can be obtained using the diffuse reflectance technique. The samples are usually dispersed in an alkali halide powder, however, to obtain more scattering and a better SNR.

It is well known that the K-M function is applicable for quantitative analysis over a limited concentration range. Hecht (83,84) has attempted to isolate the factors which are responsible for the breakdown of the K-M function. He discussed some alternative methods which would be useful to interpret the reflectance data over an increased concentration range. These methods attempt to correct for the anisotropic factor of scattering in dense samples. This approach extends the concentration range that can be studied by diffuse reflectance but is too cumbersome for routine use.

In the past, several types of devices have been used for collecting diffusely reflected light (85-89). Griffiths (82) reports that the hemiellipsoidal and ellipsoidal types of devices are the most efficient for collecting and transmitting the diffuse radiation to the detector. A liquid nitrogen cooled Mercury cadmium telluride (MCT) detector is recommended, because it allows the spectra to be collected in under five minutes with very good SNR.

Krishnan et al (90) have obtained the spectra of several solid samples such as aspirin, coal, and cement using diffuse reflectance. Spectra of these types of samples are very difficult to obtain by any other technique. The spectra of these samples obtained using the KBr grinding technique have been compared with spectra obtained using a Digilab diffuse reflectance attachment. In all cases the diffuse reflectance spectra showed more detail than those spectra obtained by grinding the samples in KBr. Kunath (91) has demonstrated that it is possible to obtain spectra of a coupling agent (γ-methacryloxypropyl-trimethoxy silane) on glass fibers. The intense absorption of light by the strong Si-O vibrations of the glass give rise to a weak diffuse reflectance below 1500 cm^{-1}. The C-H stretching bands near 2900 cm^{-1}, the C=O band at 1720 cm^{-1}, and C=C band at 1640 cm^{-1} of γ-MPS are present. In our laboratory, work involving the study of coupling agents on E-glass mats by diffuse reflectance using a Digilab attachment has been done, (see figure 5). Similar results to those of Kunath were obtained. Peaks are clearly visible above 1500 cm^{-1} where the Si-O vibration of the glass does not strongly absorb radiation. Note that the SNR is high.

The Diffuse Reflectance technique has good sensitivity and can be used for micro-sampling (92). Spectra of high quality can be obtained quickly with little sample preparation. But diffuse reflectance also has several disadvantages: 1) it is necessary to keep the particle size constant for quantitative results; 2) the concentration range of quantitative results is limited by anisotropic scattering of particles; 3) the depth of penetration is wavelength limited; and, 4) strongly absorbing modes destroy sensitivity in those overlapping regions of the spectrum, like glass fibers below 1500 cm^{-1}.

IV. Emission Spectroscopy

The high sensitivity of the FT-IR technique allows one to study emission from a sample. Several early studies (93-96) showed that the IR emission spectra could be used to identify samples that were heated [see figure 2(g)]. For a sample to be in thermal and radiative equilibrium with the environment, the amount of radiation adsorbed is equal to the amount of radiation emitted. This is given by Kirchoff's Law (97) which states that, at a given temperature, the absorbance, a, of a sample is equal to its emissivity, e. The emission depends only on the temperature of the sample. This type of radiation is called blackbody radiation. The emission spectra of a sample should be directly related to its absorbance spectra.

In practice, real objects never comply to the laws of blackbody radiators. These are three processes which occur preventing an object from being a blackbody radiator (98). Some of the incident radiation may be: 1) adsorbed, a; 2) reflected, r; or, 3) transmitted, t. The sum of these factors must add up to one:

$$a_\lambda + r_\lambda + T_\lambda = 1$$

Kirchoff's Law relates absorbance to emission:

$$\varepsilon_\lambda = a_\lambda = 1 - (r_\lambda - T_\lambda)$$

Therefore, in order to have a perfect blackbody, the material would have to be opaque and nonreflective.

In practice, the emission spectrum is usually measured from a hot sample to a cooler detector. All emission spectra must be ratioed to the energy emitted by a blackbody at the same temperature as that of the sample (99). No sample can emit more energy than a blackbody at a given temperature. The emissivity, e, is calculated by ratioing the energy emitted by a sample at any frequency to the energy emitted by a blackbody at the same frequency and temperature (100).

In IES, any background emission from the instrument (mirrors, beamsplitter, interferometer, etc.) will distort the spectrum. A four-measurement experiment has been developed to remove the background emission (101). The correction involves measuring the spectra of both the sample and blackbody interference at two temperatures. When a room temperature triglycine sulfate (TGS) detector is used, the four-measurement background correction experiment is not necessary. But the background correction is needed if a liquid nitrogen cooled Mercury cadmium telluride (HgCdTe) detector is used.

A number of materials have been used to model blackbody sources for the reference material (99,102-104). However, none of these methods of producing a blackbody reference has been established. The most recently recommended method is to coat an aluminum cup with an Epley-Parsons solar black lacquer paint which has an emittance of greater than 98% over the mid-infrared spectral range (101).

The sample being studied is usually mounted on a metal plate [figure 2(g)]. The metal support must be highly polished so that very little emission is obtained from the support. The support and sample are heated together and the emission spectrum is obtained. Both thick and thin films can be studied by this technique, but it is better suited for thin films. Thermal gradients usually arise in thick films and cause distortions in the resulting spectrum. A pure emission spectrum can originate only if the sample is at a uniform temperature throughout. In the case of thick samples (105) the temperature gradients lead to partial reabsorption of the emission band causing distortion of the peaks. This problem can be avoided if a properly designed heating cell that heats the sample from the front so that the outer layers are at the highest temperature is used. Also, by varying the intensity of the heating radiation, different thicknesses of the sample can be probed (106).

Greenler (107) has reported the theoretical considerations for studying thin films (overlayers) on highly reflective metal surfaces. Baungunten (108) demonstrated that optical interference effects caused the emission spectrum of overlayers to differ from those of the same thickness obtained by transmission. For very thin films (much less than a wavelength) perpendicular to the metal surface, no emission spectrum is obtained. At high angles from the normal, the emission should be strong. The angular dependence of emission spectral intensities has been verified (100,109). This angular dependence is analogous to that observed in the RAS technique (36,37). In a similar manner, the changes in polarized light can be related to changes in the dipole moment of the molecule perpendicular to the metal surface.

Emission studies can be carried out with very samll temperature differentials (4°C) between the sample and the detector (101) and with the increased sensitivity and lower noise level of FT-IR. The first FT-IR emission spectra were reported by Low and Coleman (95,110), including the spectra of polystyrene and nylong. Griffiths (105) then reported the potential of FT-IR for emission studies. The emission spectra can be obtained from FT-IR without heating the sample and using a low temperature detector (111,112). A major area of interest for emission spectroscopy is that of thin films and coatings on metal surfaces. Many of these examples are reviewed by Bates (112).

Other applications (104) include the emission spectra of polymer films such as polyvinylchloride, mylar, polyethylene-polyvinylacetate, and the polymeric coatings on beer cans. The degree of cure of the beer can coating was determined from the emission spectra. To show the scope of Emission Spectroscopy with the air of FT-IR, the following reported applications are mentioned. IR-emission spectroscopy has been used to monitor gaseous air pollutants (113,114). Several studies have also appeared of adsorbed species on metal surfaces (115,116)

where the heating of the sample is ideal to study the decomposition of the catalysis and their interaction with the reactants. Aronson et al (117) have developed the theory of emittance for fibrous materials. They have successfully demonstrated that, for polypropylene fibers, the experimental results confirm the validity of the theory.

V. Transmission Spectroscopy

Of all the specialized infrared sampling techniques now available to study the surface species of polymers, transmission remains the most popular for samples which can be prepared in a transparent form. Naturally, the transmission mode cannot be used to analyze opaque samples. The advent of FT-IR spectrometers has greatly aided the IR studies of polymer materials. Due to the quantitative nature of the transmission measurements, transmission is always the preferred technique to study a sample in the infrared region. If the transmission technique cannot be used, however, then one must resort to one of the above techniques.

The comparison of FT-IR spectrometers to dispersive spectrometers has been well documented by Griffiths (118) and Koenig (119). The FT-IR spectrometer is built around the Michaelson interferometer. All of the spectral information is collected in an interferogram from a single scan of the movable mirror in the interferometer. The interferometer contains no slits so the amount of energy received by the detector may be 80 to 200 times greater in an FT-IR instrument. The frequency is monitored by a laser in the FT-IR spectrometer to an accuracy of better than 0.01 cm^{-1}. This allows one to signal average the scans to the SNR can be improved.

The dedicated minicomputer greatly aids in the study of surface phenomena. The ability to subtract two absorbance spectra opened a whole new area for the transmission study of solids. If the absorbance spectra of a bulk sample can be obtained as well as the spectra of the same bulk sample which has been

surface modified, the spectral subtraction technique can be used to remove the contributions of the bulk phase. This method allows one to observe the effect of the surface treatment. The surface species can also be quantitatively determined. Spectral subtraction routines are the most widely used data manipulation programs in FT-IR. The literature shows that the subtraction routines are used in nearly every study that involves polymers. The bases of these programs have been developed by Koenig et al (119-121) and Hirschfield (122), and reviewed by Coleman and Painter (72).

Many techniques are available to prepare polymer samples for FT-IR transmission measurements. These include KBr pellet technique, mulls, solvent casting techniques, and pressing the material into transparent wafers or self-supporting thin films. The major requirement for surface and interfacial studies is that the sample preparation step leaves the chemical nature of the sample unchanged. This requirement is often the limiting factor in the study of surface species. The number of new sampling techniques which have been developed to overcome specific problems when the sample cannot be studied by transmission emphasizes the importance of this requirement. The transmission absorbance FT-IR technique is the technique of choice to study polymer samples, but if this proves unsuccessful, then another sampling technique must be used.

Glass reinforced plastics and other composite materials are some of the major areas of polymer interfacial studies today. It has been known for many years that the mechanical properties of composite materials are enhanced when coupling agents are applied to the surface of the glass fibers. The coupling agent is viewed as an adhesion promoter that chemically links the glass reinforcement material to the polymer matrix. These composite systems are of interest because the wet strength of composites is superior when a coupling agent is present. The most widely studied coupling agents to date are:

γ-aminopropyltriethoxysilane (γ-APS) (123-125), γ-methylpropylmethacrylsilane (γ-MPS) (126), vinylsilane (VS) (127-129), and others (128-130).

High surface area materials must be used even with FT-IR studies, so that enough coupling agent is present to be detected. For example, monolayer coverage of a silane was detected on a high surface area cab-o-sil (125). The results showed evidence that a chemical bond had formed between the coupling agent and the glass. Similar studies using E-glass fibers (123-126,128,129) have shown that multilayers of siloxanes have formed and the number of layers formed is concentration dependent. When E-glass fibers were used (due to multilayer formation) no direct evidence of the chemical bonds between the coupling agent and glass was seen, however.

Other studies have focused on the coupling agent matrix interface (128). It was observed that a copolymerization occurred at the interface of the amino-silane coupling agent and polyester matrix between the γ-MPS and styrene monomers in the resin matrix. Chiang and Koenig (131,132) have studied the silane-matrix interface of aminosilane-epoxy system. In both studies the results indicated that a chemical reaction occurred between the coupling agent and the matrix resin. It was found that a stronger reaction occurred when a secondary amino-silane (*N*-methylaminopropyltriethoxysilane) (MAPS) was used instead of a primary aminosilane. It is believed that the MAPS catalyzes the reaction at the inter-face.

FT-IR has also been used to study the hydrothermal stability of the coupling agent interphase. Three silanes, γ-MPS, VS, and CS (cyclohexysilane) have been studied (129,133). After 600 hours of exposure to water at 80°C, major hydrolysis in the silane interphase was observed. This indicates that the interphase is easily hydrolyziable and desorbs. The surface layers remain intact, however, if the silane is copolymerized with the matrix resin. The mechanism for this

reaction is not known, but may be related to some type of interpenetrating network that forms between the coupling agent and resin matrix.

A new area of interest in the study of fiber reinforced composites is the interaction between silanes on particulate fillers. When high surface area fillers are used, they can be pressed into KBr pellets and studied by the transmission method. The diffuse reflectance technique appears to be particularly well suited for this type of study, however, because the fillers are in a powdered form. Both techniques are currently being used in our laboratory to study coupling agent filler interfaces (134).

VI. Conclusions

The new techniques that have recently been developed for the infrared region of the spectrum have made an already popular technique much more versatile for the study of solid materials such as polymers. The use of FT-IR instruments allows one to routinely study the vibrational properties of surfaces and interfaces. Naturally, not every sample can be studied by the transmission method, but enough techniques are available that most samples can be studied by infrared spectroscopy. The proper choice of the IR sampling technique is the most important decision to be made in order to obtain useful, interpretable spectra of the vibrational modes and chemical structure of the sample. This review has highlighted the potential applications of each of the techniques discussed, and pointed out the differences between them in order to help one make such decisions. It is clear that the field of FT-IR analysis of polymers will continue to grow in the near future due to the versatility of this technique.

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Figure Captions

Figure 1 Shows the effect of refractive index on light as a function of angle of incidence. Transmission at 90°, reflection and refraction at $\Theta = \Theta_c$, and total internal reflection at $\Theta > \Theta_c$.

Figure 2(a) PAS cell, the incident light produces pressure fluctuations which are detected by a sensitive mircophone.

(b) Single reflection RA set-up. Light penetrates the sample first and is reflected by the metal mirrors (Θ should be 70 to 89.5°).

(c) Multiple reflection RA set-up. Light penetrates the sample first and is reflected by the metal mirrors (Θ should be 70 to 89.5°).

(d) Single reflection IRS set-up. Light passes through the IRE first and is totally reflected at $\Theta > \Theta_c$.

$$n_1 \sin\Theta_c = n_2 \sin 90°$$

$$\sin\Theta_c = n_2/n_1$$

(e) Multiple reflection IRS set-up.

(f) Diffuse reflectance, the scattered light is collected by mirrors and directed to the detector.

(g) Emission technique, the sample is heated and the emitted radiation is analyzed.

(h) Transmission spectroscopy.

(i) Spectral reflection (mirror-like), angle of incidence equals angle of reflection.

Figure 3(A) Transmission infrared spectrum of undecylimidazole in KBr pellet.

(B) Reflection-absorption infrared spectrum of undecylimidazole on gold mirror withdrawn from 10g/l ethanol solution. (From ref. 63.)

Figure 4 Reflectivity versus angle of incidence for an interface between media with indices, $n_1 = 4$ and $n_2 = 1.33$, for light polarized perpendicular, R, and parallel, R, to plane of incidence for external reflection (solid lines) and internal reflection (dashed lines). θ_c, θ_B, and θ_p and the critical, Breweters', and principal angles, respectively. (From ref. 32.)

Figure 5 Diffuse reflectance spectra of γ-APS (top) and γ-MPS (bottom) on E-glass mats; the contribution of glass was subtracted out.

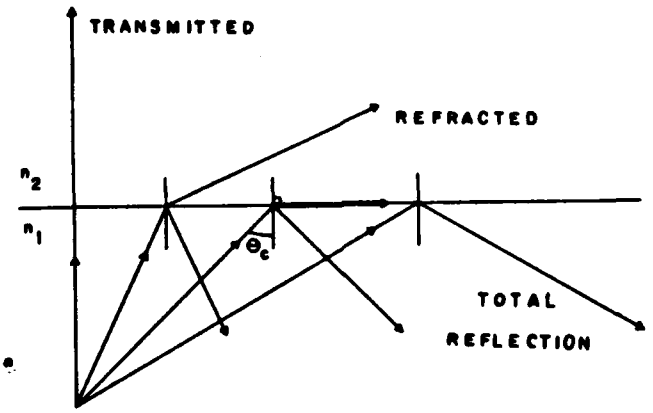
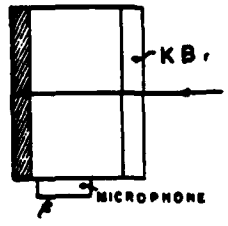
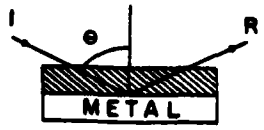


Figure 1

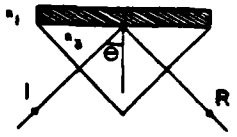


(a)



(b)

(c)



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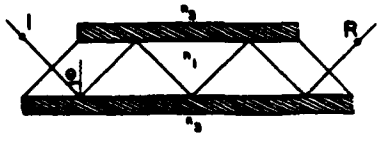
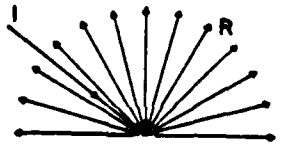
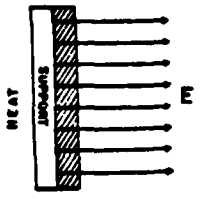


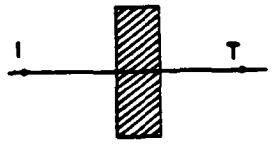
(e)



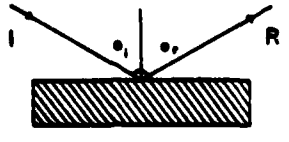
(f)



(g)



(h)



(i)

Figure 2

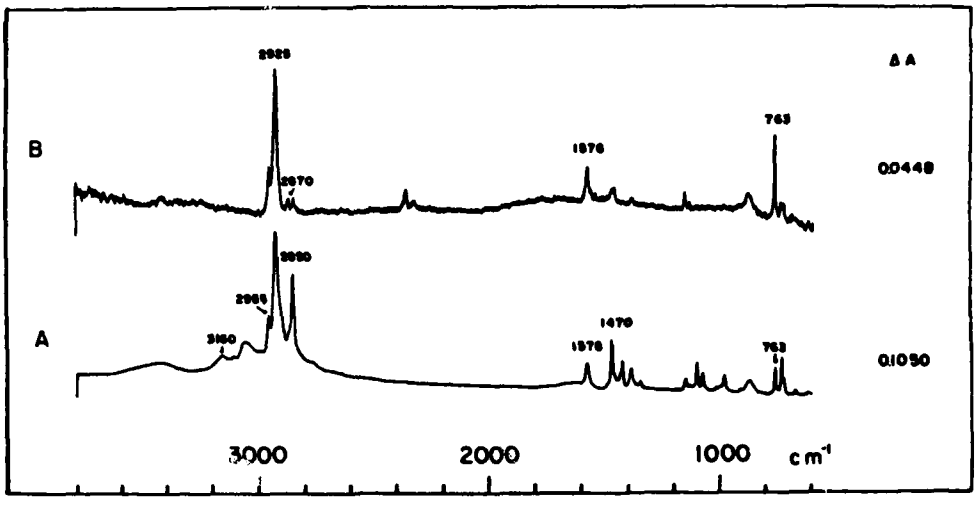


Figure 3

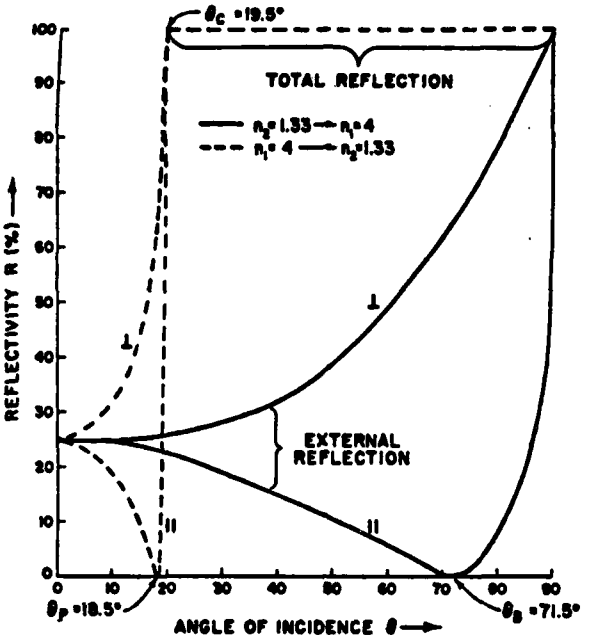


Figure 4

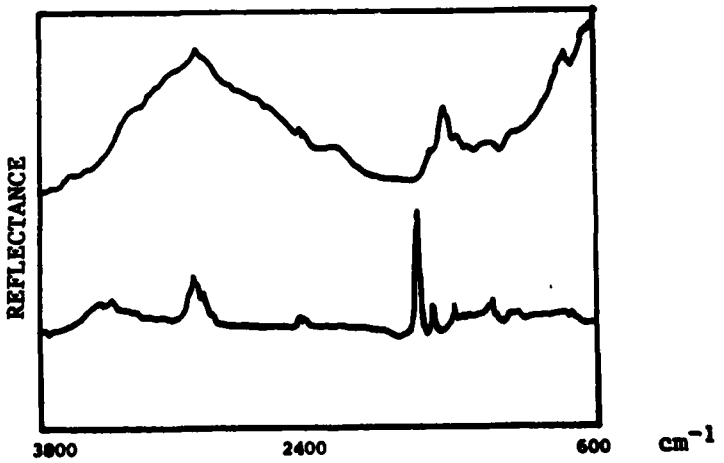


Figure 5